THE EFFECT OF MOLYBDENUM, TUNGSTEN, AND VANADIUM ON THE ANNEAL HARDENING OF COLD WORKED 18Cr-12Ni STAINLESS STEEL

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16. Abstract

The effect of alloying elements on mechanical properties of cold-worked 18Cr-12Ni stainless steel is examined. The hardness and spring limit of 18Cr-12Ni stainless steel, soft in solution-treated condition, increases with increase of cold reduction. Low-temperature annealing after cold work increases the spring limit. Substitutionally dissolved ferrite-forming elements -- molybdenum, tungsten and vanadium -- improve mechanical properties of steel, though relatively slightly in cold work and subsequent annealing condition. Addition of molybdenum is most effective, with a spring limit of 100 kg/mm^2 after annealing at 500°C after 90% reduction. Other mechanical properties of this steel are also improved by this treatment, a hardness of 500 DPN and tensile strength of 170 kg/mm^2 being obtained.

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THE EFFECT OF MOLYBDENUM, TUNGSTEN, AND VANADIUM ON THE ANNEAL HARDENING OF COLD WORKED 18Cr-12Ni STAINLESS STEEL

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I. Introduction /346*

The authors previously reported that, when 18Cr-12Ni stainless steel is given powerful cold working and a suitable heat treatment, it will display spring properties comparable to those of beryllium steel. Furthermore, the magnetic permeability will not exceed 1.02 (300 Oe). Therefore, it is useful as a nonmagnetic spring material [1, 2]. Here are reported the results obtained when it was dissolved in austenite and when molybdenum, tungsten, and vanadium, which were expected to increase the strength [3, 4], were each added individually for the purpose of improving the mechanical properties and the spring properties. The effects after cold working and low-temperature annealing were investigated.

II. Specimens and Experimental Methods

The chemical analyses of the specimens used in these experiments are shown in Table 1. The method for preparing the specimens was the same as that in the previous report [1]. After heating in a vacuum high-frequency furnace, they were given annealing, hot rolling, solution heat treatment, and cold rolling. The thickness of the test pieces was 0.5 mm.

For the mechanical properties, the Vickers hardness, the tensile strength, and the Young's modulus were measured. For the

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* Numbers in the margin indicate pagination in the foreign text.

TABLE 1. CHEMICAL ANALYSES OF EXPERIMENTAL STEELS (wt-%)

Steel	C	Si	Mn	Cr	Ni	Mo	W	V
C-1	0.090	1.02	1.75	18.52	11.93	—	—	—
M-1	0.120	1.18	1.63	16.59	12.36	2.13	—	—
M-2	0.101	1.18	1.19	17.15	11.89	2.86	—	—
M-3	0.101	1.28	1.52	16.85	11.92	4.37	—	—
W-1	0.105	0.90	1.45	17.95	12.01	—	1.50	—
W-2	0.092	0.97	1.55	17.72	11.72	—	3.22	—
W-3	0.101	0.95	1.57	17.73	11.92	—	5.91	—
V-1	0.119	0.90	1.66	17.91	11.43	—	—	0.57
V-2	0.121	0.93	1.42	18.04	11.60	—	—	1.55

spring properties, the spring limit (Federbiegegrenze) as prescribed in DIN 50 151 was measured using a Siemens tester. Test pieces 10 mm wide and 200 mm long were supported at two points and pressed down at the center in order to deflect them. The deflection was gradually increased, and the value was indicated in terms of the maximum surface stress when there was a permanent set of 0.05 m after the stress had been removed. The appearance and a diagram of the tester are shown in Photo 1 and Fig. 1. The /347
magnetic permeability was measured with a ballistic galvanometer type fluxmeter with a magnetic field intensity of 300 Oe.

III. EExperimental Results and Discussion

1. Mechanical Properties

The relationships between the reduction of area by cold working on the one hand and the hardness and tensile strength on the other are shown in Fig. 2. As the reduction of area increases, naturally there is also an increase in the hardness, but at a reduction of area greater than 50%, the rate of hardening by working is relatively small. When molybdenum is added at the cold worked state, there is a slight increase in the hardness, but addition of tungsten and vanadium has no effect. Specimens given 90% cold working all had a hardness of 400-450 DPN. Since there is almost no formation of martensite as a result of cold working of 18Cr-12Ni stainless steel [5], the hardening is probably caused chiefly by work hardening. Since molybdenum, tungsten, and vanadium are all ferrite-forming elements, it is believed that specimens to which these elements have been added will tend to produce martensite as a result of cold working more easily than in the case of C-1. However, on the basis of the results in Fig. 2, when there are additions of approximately this amount, there is solid solution in the austenite, and the so-called solid solution hardening effect can be observed to a certain degree. However, it would be inconceivable that any martensite sufficient to make a contribution to the hardness could be produced by cold working.

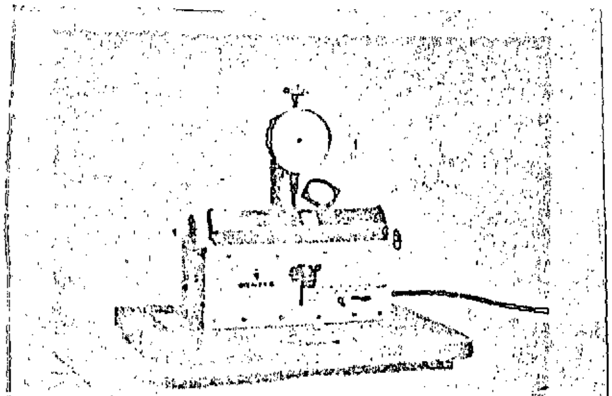

Photo. 1 Appearance of spring tester.

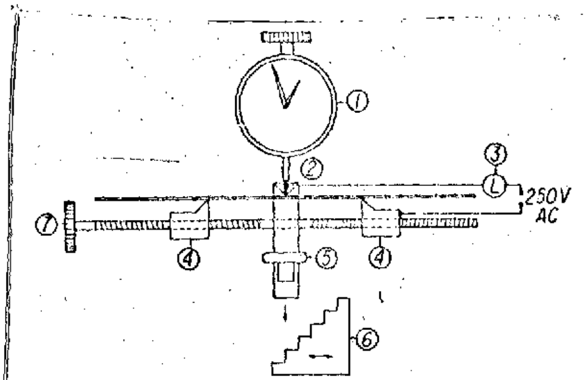

Fig. 1 Schematic view of spring tester; (1) dial gauge, (2) contact point, (3) glow lamp, (4) knife edge, (5) loading key, (6) steps for strain adjustment, (7) span adjustment screw.

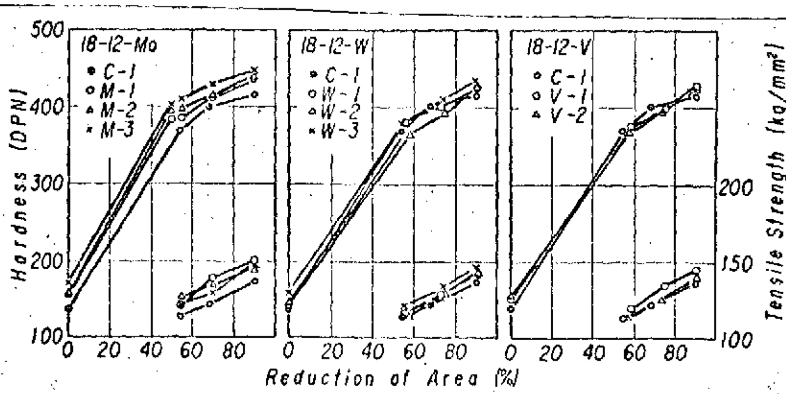

Fig. 2 Effect of cold working on hardness and tensile strength of 18-12 stainless steels.

The tensile strength also rises as the reduction of area in cold working increases. Addition of molybdenum, tungsten, and vanadium increases the tensile strength, and in each case as the amount added is increased, there are increases in the tensile strength. The tensile strengths of samples given 90% cold working are 140 kg/mm^2 for C-1 and 145-150 kg/mm^2 for those to which molybdenum, tungsten, and vanadium were added.

In Fig. 3 are shown the changes in hardness following low-temperature annealing of specimens which have been given 90% cold working. The hardness increases with the increase in the annealing temperature, and in all cases there is a maximum value at 500°C.[1] When the temperature exceeds 500°C, there is softening on account of the recrystallization, but the Mo-series and W-series soften less easily than the C-1 and V-series. In all cases, the addition of molybdenum, tungsten, and vanadium is effective in increasing the hardness after low-temperature annealing. When molybdenum and tungsten are added, increases in the amounts added are followed by increases in the hardness as well. However, when a certain amount of vanadium is added, the hardness reaches its maximum value, and if any further amounts are added, the hardness will decline. It is believed that this is because

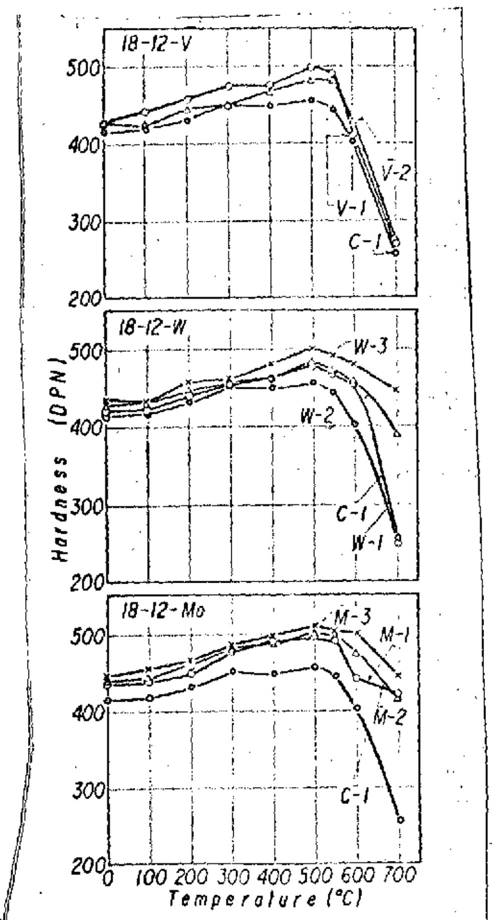

Fig.3 Relation between annealing temperature and hardness of cold rolled steels.

[1] We wish to discuss the mechanism of low-temperature annealing hardening in our next report.

vanadium tends to form carbides readily. The carbides are supposedly precipitated on the crystal grain boundary and reduce the effect of the solid solution hardening. When we compare the effects of addition of molybdenum, tungsten, and vanadium at the identical /348
at-%, the highest hardness obtained is that of M-2 (500 DPN). That of W-3 is 500 DPN, and that of V-2 is 485 DPN. Molybdenum and tungsten have approximately the same effect, and vanadium is somewhat inferior.

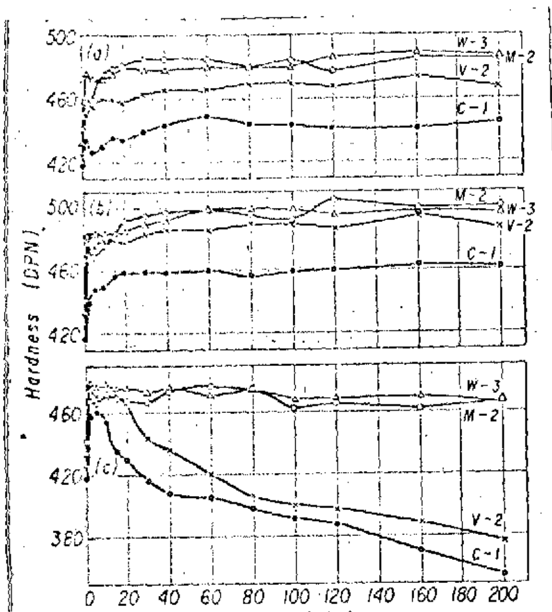

Fig.4 Time-hardness curves of cold rolled steels, annealed at (a) 400°, (b) 500°, (c) 600°C after 90% reduction.

In Fig. 4 are shown time-hardness curves for specimens given 90% cold working when they were annealed at 400°, 500°, and 600°C, respectively. At 400° and 500°C, in all cases the hardness increased rapidly several minutes after heating, displayed a tendency towards saturation or decrease, and then once again rose, reaching a saturation value in 60-100 min. At 600°C, there was a rapid increase several minutes after heating; after the maximum value had been reached, there was gradual softening. Specimens to which molybdenum and tungsten had been added had extremely slow softening in comparison with low C-1. This, it is believed, indicates that when 18Cr-12Ni stainless steels are used for springs, addition of molybdenum and tungsten is effective in cases where a certain degree of heat resistance is necessary. It was also learned from these results that a retention time of 1 hour is sufficient for low-temperature annealing.

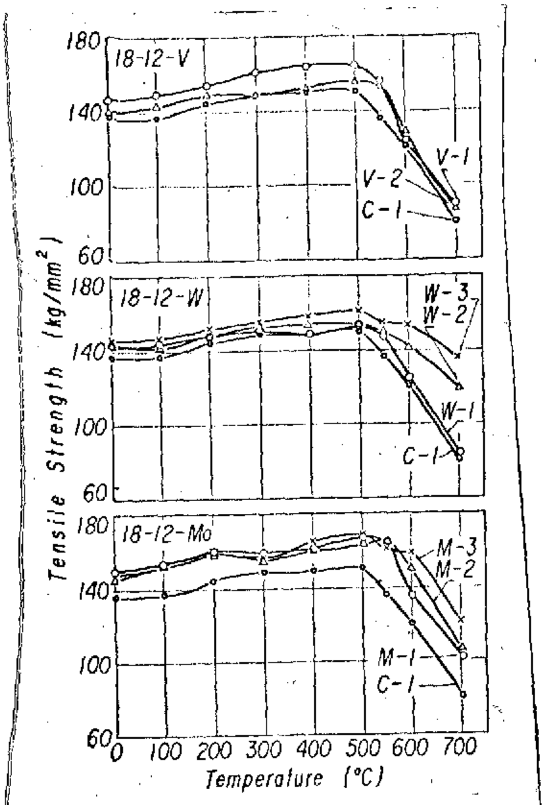

Fig.5 Relation between annealing temperature and tensile strength of cold rolled steels.

Fig. 5 shows the changes in the tensile strength caused by low-temperature annealing in specimens given 90% cold working. The relationship between the tensile strength and the annealing temperature has approximately the same tendency as the relationship between the hardness and the annealing temperature. In every case, the maximum tensile strength is that which occurs in annealing at 500°C. The increase is approximately 10-20 10-20 kg/mm^2, and there are no differences even when additive elements are present. The addition of molybdenum, tungsten, and vanadium is effective in increasing the tensile strength in the annealed state, and in every case there was an increase of about 10 kg/mm^2 when they were added at 1.5 at-%.

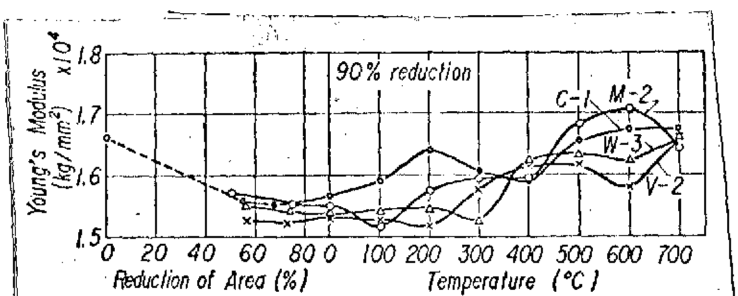

Fig.6 Change of Young's modulus of 18-12 stainless steels by cold rold rolling and low temperature annealing.

Fig. 6 shows the changes in the Young's modulus caused by cold working and by low-temperature annealing. The Young's modulus was sought from the deflection when a known weight was applied on one end of a cantilever, in the same way as in the previous report [1][2]. The Young's modulus tended to decline

[2] The lengthwise direction of the test pieces was parallel to the rolling direction.

as a result of cold working, and low-temperature annealing caused it to increase, although there were complicated changes in this case. This coincides well with the results obtained by Izumi et al. [6] with nickel silver. The addition of molybdenum, tungsten, and vanadium also brings about decreases in the Young's modulus. When specimens were annealed for 1 hour at 500°C after having been given 90% cold working, their Young's modulus was approximately 16,500 kg/mm^2.

2. Spring Properties

We reported in a previous paper [1] that the spring limit of 18Cr-12Ni stainless steel underwent few changes in cold working, but was remarkably raised by low-temperature annealing. However, the ultimate value reached after low-temperature annealing will be higher the greater is the reduction of area by cold working. Thus, we first investigated the relationship between the reduction of area by cold working and the srping limit value. The results are shown in Fig. 7. In /349 every case, the spring limit rises as the reduction of area increases. The addition of molybdenum, tungsten, and vanadium also improves the spring limit value. Next, in Fig. 8 we show the changes in the spring limit value accompanying low-temperature annealing of specimens which have undergone 90% cold working. The spring limit value increases remarkably as the annealing temperature is raised. In

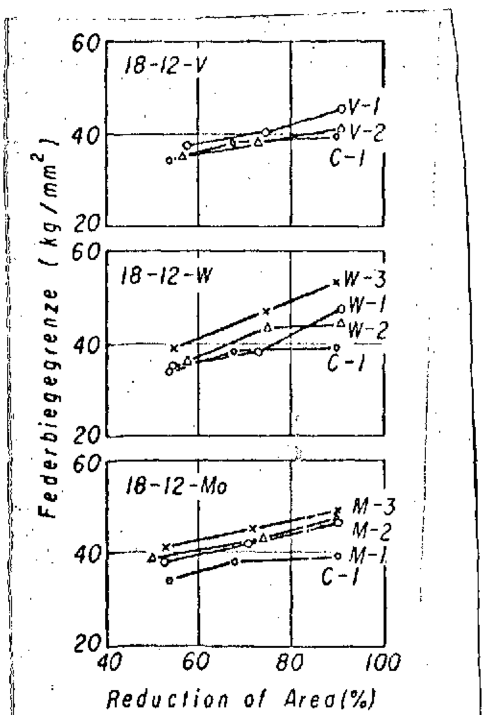

Fig.7 Effect of cold working on Federbiegegrenze of 18-12 stainless steels.

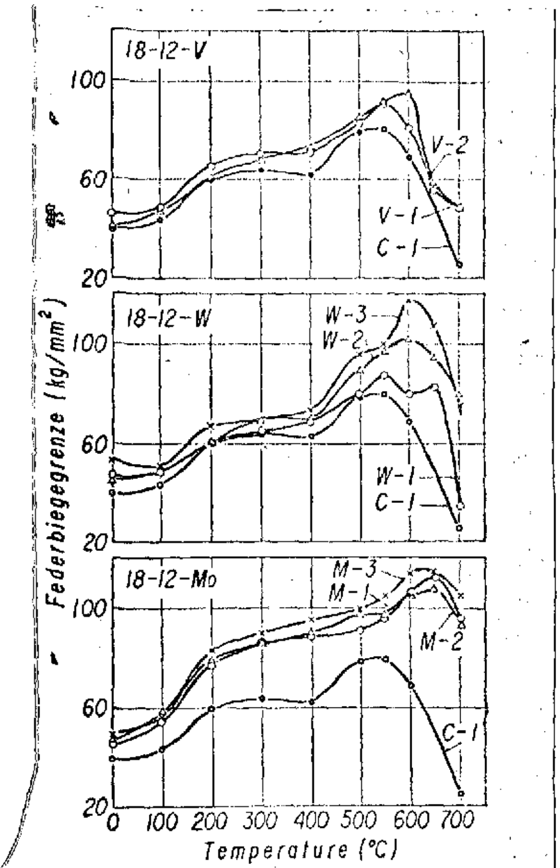

Fig. 8 Relation between annealing temperature and Federbiegegrenze of cold rolled steels.

M-2 it reaches its maximum at 650°C, and in W-3 and V-2 at 600°C. The value is 107 kg/mm^2 in M-2, 117 kg/mm^2 in W-3, and 94 kg/mm^2 in V-2. In comparison with C-1, the value for M-2 is 30 kg/mm^2 higher, the value for W-3 is 40 kg/mm^2 higher, and the value for V-2 is 15 kg/mm^2 higher. Thus, the addition of all three elements, molybdenum, tungsten, and vanadium, is effective, and molybdenum and tungsten are both especially effective.

Generally speaking, when cold-worked austenitic stainless steels are given low-temperature annealing, there is a pronounced rise in the spring limit as compared with the hardness and the tensile strength [7]. The spring limit value corresponds to the yield strength in tension testing, as is clear from the measuring method. Therefore, the pronounced increase caused by low-temperature annealing is understandable. Furthermore, the annealing temperature at which the spring limit reaches its maximum value is 600°-650°C, which is higher than that for C-1. This is also more than 100°C higher than the temperature at which the hardness and the tensile strength reach their maximum values. The cause of this is unclear. However, when heating is performed for a long time at temperatures in the vicinity of 600°C, carbides are precipitated on the grain boundary, and this causes grain boundary corrosion [8]. Therefore, it is is believed necessary for the annealing temperature in actual practice to be less than 500°C when one takes into consideration the corrosion resistance as well.

3. Magnetic Properties

In Table 2 are shown the changes in the magnetic permeability μ in specimens given 50%, 70%, and 90% cold working when they were annealed for 1 hour at intervals of 100°C within the range of 100-600°C. In the "as-rolled" state, the magnetic permeability increases slightly as the reduction is increased in all cases. This indicates that martensite was produced by cold working. The addition of molybdenum does not affect the magnetic permeability, but the addition of tungsten and vanadium increases the magnetic /350
permeability. It is believed that this is so for the following reasons. That is, because tungsten and vanadium are strong ferrite-forming elements, addition of them makes the austenite less stable than in C-1, and martensite tends to be produced more easily as a result of cold working. On the other hand, the magnetic permeability is almost unchanged as a result of low-temperature annealing. Cina [9] states that the martesnite in 18Cr-8Ni stainless steel produced by cold working is transformed into austenite at temperatures of 500÷800°C. Imai et al. [10] also investigated the changes in the magnetic properties accompanying the heating of 18Cr-8Ni stainless steel which had been given cold working. They report that they begin to lose their magnetic properties suddenly in the vicinity of 500°C. The reason why the results of measurements of the magnetic permeability in these experiments are more or less constant within the range of 100-600°C is not clear, although it is supposed that this may be because the martensite produced by cold working is extremely stable in the 18Cr-12Ni stainless steels and transformations do not commence until the temperature is greater than 600°C, or perhaps because the austenite caused by heating changes back into martensite as the temperature is lowered.

TABLE 2. EFFECT OF COLD WORKING AND LOW-TEMPERATURE ANNEALING ON MAGNETIC PROPERTY OF 18Cr-12Ni STAINLESS STEEL

Steel	Cold reduction (%)	Permeability ($H=300$ Oe)						
		As roll	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C
C-1	50	1.020	1.011	1.006	1.005	1.006	1.006	1.009
	70	1.027	1.013	1.011	1.007	1.007	1.011	1.011
	90	1.035	1.030	1.026	1.019	1.021	1.009	1.013
M-2	50	1.018	1.012	1.010	1.009	1.007	1.009	1.009
	70	1.009	1.009	1.010	1.007	1.004	1.011	1.007
	90	1.028	1.022	1.025	1.019	1.021	1.013	1.013
W-3	50	1.49	1.49	1.51	1.49	1.51	1.49	1.43
	70	1.75	1.75	1.75	1.76	1.72	1.73	1.68
	90	1.93	1.92	1.94	1.90	1.93	1.90	1.85
V-2	50	1.051	1.049	1.062	1.052	1.067	1.060	1.046
	70	1.13	1.17	1.13	1.17	1.13	1.10	1.066
	90	1.52	1.60	1.58	1.61	1.64	1.48	1.32

IV. Summary

The effects of molybdenum, tungsten, and vanadium on the properties of cold-worked 18Cr-12Ni stainless steel were investigated, and the following results were obtained.

(1) The addition of molybdenum and tungsten improves the spring properties and the mechanical properties. When vanadium is added, the properties do not always improve when the amount added is increased, and the maximum value is displayed when a certain amount is added.

(2) When molybdenum, tungsten, and vanadium are added, the spring limit reaches its maximum value in annealing at 600-650°C, but the hardness and tensile strength reach their maximum values at 500°C and do not differ from cases when these elements are not added.

(3) When molybdenum, tungsten, and vanadium are added, the Young's modulus decreases in all cases.

(4) The magnetic permeability increases slightly as the reduction of area by cold working increases, but there are almost no changes in it in low-temperature annealing at temperatures up to 600°C. The addition of molybdenum, has no effects on the magnetic permeability, but the addition of tungsten and vanadium increases the magnetic permeability. Consequently, the addition of tungsten and vanadium is undesirable from the viewpoint of non-magnetic spring materials.

(5) The optimum low-temperatureaannealing conditions for M-2 specimens are 500°C for 1 hour when the corrosion resistance is taken into consideration. Ninety-percent cold rolled specimens treated under these conditions had a hardness of 500 DPN, a tensile strength of 165 kg/mm^2, a Young's modulus of 16,900 kg/mm^2, and a spring limit value of 100 kg/mm.

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